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I, GAYE TURNER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 9571 for a patent by SILVERBROOK RESEARCH PTY. LTD. filed on 21 August 2000.

WITNESS my hand this  
Fourteenth day of August 2001

A handwritten signature in cursive script, appearing to read "G. Turner".

GAYE TURNER  
TEAM LEADER EXAMINATION  
SUPPORT AND SALES

CERTIFIED COPY OF  
PRIORITY DOCUMENT



# AUSTRALIA

Patents Act 1990

## Provisional Specification

for invention entitled:

INFRARED INK COMPOSITION (INK03A)

The invention is described in the following statement: -

## **FIELD OF THE INVENTION**

The present invention relates to compounds that consist of molecules that are suitable for use as dyes. In particular, the present invention relates to compounds that are suitable for use as infrared dyes, to compositions containing these compounds, including colour light-sensitive material, and to processes for their use as infrared absorbers. The present invention has particular application to infrared printing inks.

## **BACKGROUND**

Recently there has been renewed interest in "innovative" or "functional" dyes. One area of interest is that of optical recording technology where gallium aluminium arsenide (GaAlAs) and indium phosphide (InP) diode lasers are widely used as a light source. Since dyes absorbing in the near infrared (near-IR) region (i.e., beyond about 700 nanometers in wavelength and less than about 2000 nanometers in wavelength) are required and the oscillation wavelengths fall in the near-infrared region, they are suitable candidates for use as infrared dyes.

Infrared dyes have applications in many areas. For example, infrared dyes are important in the optical data storage field, particular in the DRAW (Direct Reading After Writing) and WORM (Write Once, Read Many) disk, which is used for recording. Currently, indolinocyanine dyes, triphenylmethane dyes, naphthalocyanine dyes and indonaphthalene-metal complex dyes are commercially available for use as organic colorants in DRAW disks. Cyanine dyes can only be used if additives improve the lightfastness.

Another application of infrared dyes is in thermal writing displays. In this application, heat is provided by a laser beam or heat impulse current. The most common type of infrared dyes used in this application are the cyanine dyes, which are known as laser dyes for infrared lasing.

Infrared dyes are also used as photoreceptors in laser printing. Some infrared-absorbing dyes are used in laser filters. They also find application in infrared photography and even have application in medicine, for example, in photodynamic therapy.

The compounds of the present invention will now be described in the context of printing inks and the like, but it will be understood by the skilled reader that the compounds described hereunder may be used in other applications, for example, those set out above.

Fast, error-free data entry is important in current communication technology. Automatic reading of digital information in printed, digital and analog form is particularly important. An example of this technology is the use of printed bar codes that are scannable. In many applications of this technology, the bar codes are printed

with an inks that are visible to the unaided eye. There are, however, applications (eg security coding) that require the barcode or other intelligible marking to be printed with an ink that invisible to the unaided eye but which can be detected under UV light or infrared light (IR).

For instance, U.S. Pat. No. 5,093,147 describes a method exploiting the process of fluorescence in which a dye is excited by ultra-violet (UV), visible or near-IR radiation and fluorescent light emitted by the dye material is detected. This reference describes a jet printing process used to apply a compatible liquid or viscous substance containing an organic laser dye that is poorly absorptive of radiation in the visible wavelength range of about 400 nm to about 700 nm, and is highly absorptive of radiation in the near-IR wavelength range of about 750 nm to about 900 nm. The dye fluoresces at longer wavelengths in the IR in response to radiation excitation in the near-IR range.

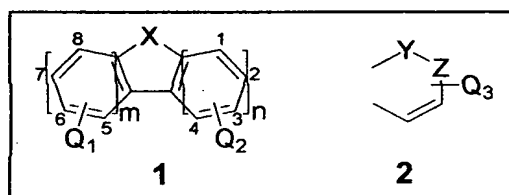
Another example is described in U.S. Pat. No. US Pat No. 5,460,646 (Lazzouni et al) which describes the use of a colorant which is silicon (IV) 2,3-naphthalocyanine bis((R<sub>1</sub>)(R<sub>2</sub>)(R<sub>3</sub>)-silyloxi) wherein R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are selected from the group consisting of an alkyl group, at least one aliphatic cyclic ring, and at least one aromatic ring.

The infrared absorbing dyes Squarylium and Croconium dyes have been extensively described in the literature (see for example, T. P. Simard, J. H. Yu, J. M. Zebrowski-Young, N. F. Haley and M. R. Detty, *J. Org. Chem.* 65 2236 (2000), and J. Fabian, *Chem. Rev.* 92 1197 (1992)). These prior art compounds have a central squarylium or croconium moiety connected to traditional electron donors. These donors act to donate an electron to the central squarylium or croconium moieties. However, these particular dyes do not absorb at a high enough wavelength and/or also absorb too strongly in the visible spectrum. Secondly, it is the infrared absorbing property of the molecule when it is not in solution that is more important in this particular application than when it is solvated. That is, whether the ratio of infrared absorption to visible absorption ( $\epsilon_{\text{ratio}}$ ) of the colorant on a surface is still acceptable for use as a security ink or like applications. This was brought into question by such groups as D. Keil, H. Hartmann and C. Reichardt, *Leibigs Ann. Chem.* 935 (1993). For example, they showed that when a croconate dye was deposited onto a polymer surface that the sharp infrared absorption peak becomes a very broad peak that contains a large shoulder in the visible part of the spectrum. This may be explained by the lack of rigidity of the molecule, which may be maintained while in a solvent, and/or that intermolecular interactions with other molecules, while not in a solvent, causes a hysochromic shift of the absorption peak. A molecular dynamics simulation of a typical squarylium dye shows that the infrared absorption peak becomes spread

out so much so that  $\epsilon_{\text{ratio}}$  decreases by about two orders of magnitude. Hence the rigidity of conventional infrared dyes needs to be addressed and/or a possible method is used to decrease intermolecular interactions when they are deposited onto a surface.

## **SUMMARY OF THE INVENTION**

Conventional croconium and squarylium dyes have absorption peaks in the near infrared part of the spectrum, typically from 700 to 900 nanometers. The croconate dyes of Simard et al (supra) actually extend up to 1081 nanometers. However, the ratio of near infrared absorption, that is absorption from 700 to less than about 2000 nm in wavelength, to visible absorption ( $\epsilon_{\text{ratio}}$ ) for the squarylium or croconate dyes is not sufficient when deposited onto a surface. We have found that an improvement of this ratio can be achieved by using a molecule that is shown as 1.



wherein m and n are the number of fused 6-membered aromatic rings connected to each side of the central moiety such that the first 6-membered aromatic ring, if present, is connected as shown in 1; and

wherein  $Q_1$  and  $Q_2$  are one of the same or different fused rings shown as 2 whereby one ring shown as 2 is connected at any of the two adjoining positions  $C_1$  to  $C_4$  at any orientation and another ring shown as 2 is connected to any of the two adjoining positions  $C_5$  to  $C_8$  at any orientation of the outer aromatic rings shown in 1 which may also include one or many substituents individually selected from the group consisting of  $R_1$ , a fused 5-membered ring or a 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from  $R_2$ , and fused polyaromatic rings optionally substituted with one or more substituents selected from  $R_3$  wherein  $R_1$ ,  $R_2$  and  $R_3$  are individually selected from the group R; and

wherein X is selected from the group consisting of CO, O, S, SO,  $SO_2$ , Se, SeO,  $SeO_2$ , Te, TeO,  $TeO_2$ ,  $CR_4R_5$ ,  $NR_4$ ,  $SiR_4R_5$ ,  $GeR_4R_5$ ,  $PR_4$  where  $R_4$  and  $R_5$ , which may be the same or different, are selected from the group R; and

wherein Y is individually selected from the group consisting of CO, O, S, SO,  $SO_2$ , Se, SeO,  $SeO_2$ , Te, TeO,  $TeO_2$ ,  $CR_6R_7$ ,  $NR_6$ ,  $SiR_6R_7$ ,  $GeR_6R_7$ ,  $PR_6$  and Z is selected from  $CR_8$  or N where  $R_6$ ,  $R_7$  and  $R_8$  which may be the same or different, are selected from the group R; and

wherein Z is individually selected from the group consisting of CO, O, S, SO,  $SO_2$ , Se, SeO,  $SeO_2$ , Te, TeO,  $TeO_2$ ,  $CR_9R_{10}$ ,  $NR_9$ ,  $SiR_9R_{10}$ ,  $GeR_9R_{10}$ ,  $PR_9$  and Y is

selected from  $CR_{11}$  or N where  $R_9$ ,  $R_{10}$  and  $R_{11}$  which may be the same or different, are selected from the group R; and

$Q_3$  and  $Q_4$  may be 0, 1 or more than 1 substituents that are individually selected from the group consisting of  $R_{12}$ , a fused 5-membered ring or a 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from  $R_{13}$ , and fused polyaromatic rings optionally substituted with one or more substituents selected from  $R_{14}$  wherein  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are individually selected from the group R; and

R is the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted thioalkyl group.

Bulky substituents are preferably used in an attempt to decrease the intermolecular interactions as these intermolecular interactions may increase the absorption of the compound in the visible part of the spectrum.

Accordingly, in a first aspect, the present invention provides an infrared dye, characterised in that the dye comprises of a molecule shown in 1.

In a second aspect, the present invention provides indicia for a substrate. The substrate may be paper, polymer, and the like. The indicia may be printed characters, shapes or the like that any machine readable instrument may detect or any visual markings that may be detected.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

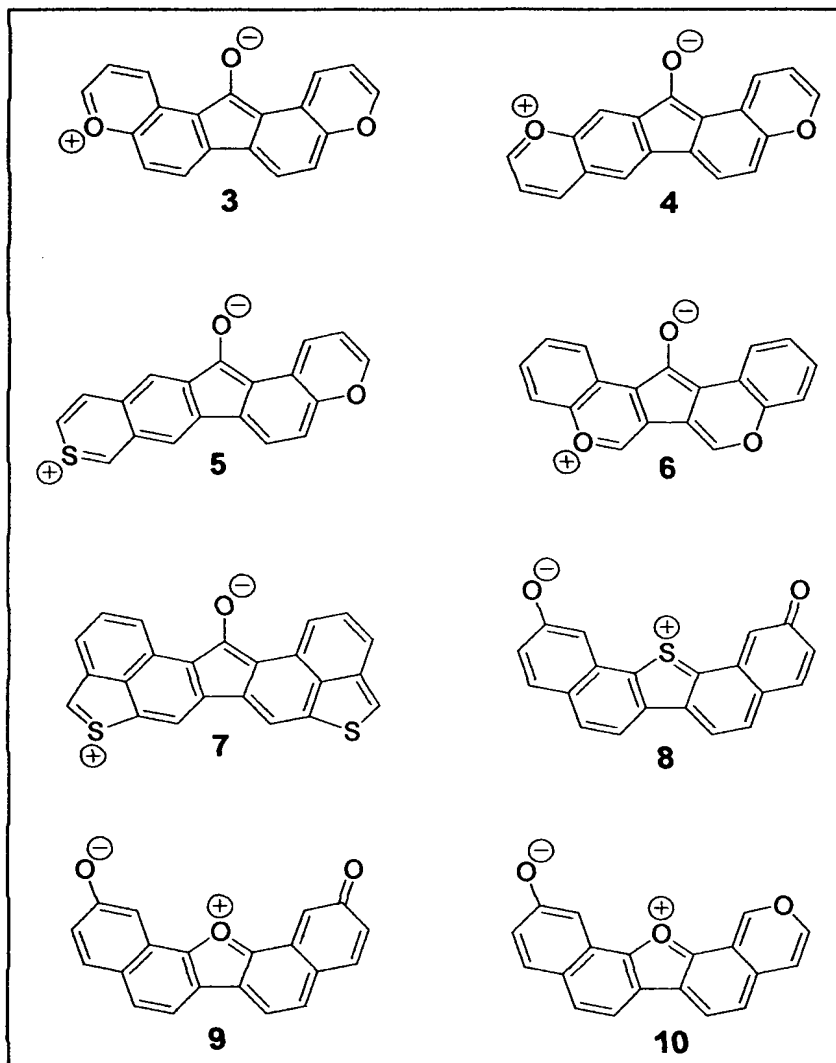
Figure 1: shows a calculated absorption spectra for 3;  
Figure 2: shows a calculated absorption spectra for 4;  
Figure 3: shows a calculated absorption spectra for 5;  
Figure 4: shows a calculated absorption spectra for 6;  
Figure 5: shows a calculated absorption spectra for 7;  
Figure 6: shows a calculated absorption spectra for 8;  
Figure 7: shows a calculated absorption spectra for 9;  
Figure 8: shows a calculated absorption spectra for 10;

## **EMBODIMENTS**

In order that the present invention may be more readily understood we provide the following non-limiting embodiments.

The formula for specific examples of dyes in accordance with the present invention are given below.

Examples of infrared dyes in accordance with the present invention comprise of the molecules **3** to **10** given below.



The absorption spectra for **3** to **10** were calculated and are given in Figures 1 to 8 respectively. As can be seen from the spectra, the molecules in accordance with the present invention have absorption peaks in the near infrared and a high value of  $\epsilon_{\text{ratio}}$ , that is  $\epsilon_{\text{ratio}}$  is larger than two.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

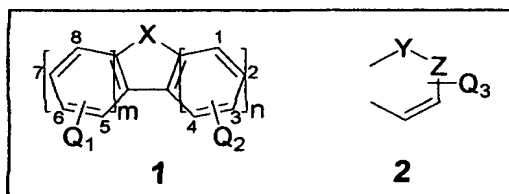
It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Dated this twenty first day of August 2000

Silverbrook Research Pty Ltd

CLAIMS:

1. An infrared dye wherein the dye comprises of a molecule 1



wherein m and n are the number of fused 6-membered aromatic rings connected to each side of the central moiety such that the first 6-membered aromatic ring, if present, is connected as shown in 1; and

wherein Q<sub>1</sub> and Q<sub>2</sub> are one of the same or different fused rings shown as 2 whereby one ring shown as 2 is connected at any of the two adjoining positions C<sub>1</sub> to C<sub>4</sub> at any orientation and another ring shown as 2 is connected to any of the two adjoining positions C<sub>5</sub> to C<sub>8</sub> at any orientation of the outer aromatic rings shown in 1 which may also include one or many substituents individually selected from the group consisting of R<sub>1</sub>, a fused 5-membered ring or a 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from R<sub>2</sub>, and fused polyaromatic rings optionally substituted with one or more substituents selected from R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are individually selected from the group R; and

wherein X is selected from the group consisting of CO, O, S, SO, SO<sub>2</sub>, Se, SeO, SeO<sub>2</sub>, Te, TeO, TeO<sub>2</sub>, CR<sub>4</sub>R<sub>5</sub>, NR<sub>4</sub>, SiR<sub>4</sub>R<sub>5</sub>, GeR<sub>4</sub>R<sub>5</sub>, PR<sub>4</sub> where R<sub>4</sub> and R<sub>5</sub>, which may be the same or different, are selected from the group R; and

wherein Y is individually selected from the group consisting of CO, O, S, SO, SO<sub>2</sub>, Se, SeO, SeO<sub>2</sub>, Te, TeO, TeO<sub>2</sub>, CR<sub>6</sub>R<sub>7</sub>, NR<sub>6</sub>, SiR<sub>6</sub>R<sub>7</sub>, GeR<sub>6</sub>R<sub>7</sub>, PR<sub>6</sub> and Z is selected from CR<sub>8</sub> or N where R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> which may be the same or different, are selected from the group R; and

wherein Z is individually selected from the group consisting of CO, O, S, SO, SO<sub>2</sub>, Se, SeO, SeO<sub>2</sub>, Te, TeO, TeO<sub>2</sub>, CR<sub>9</sub>R<sub>10</sub>, NR<sub>9</sub>, SiR<sub>9</sub>R<sub>10</sub>, GeR<sub>9</sub>R<sub>10</sub>, PR<sub>9</sub> and Y is selected from CR<sub>11</sub> or N where R<sub>9</sub>, R<sub>10</sub> and R<sub>11</sub> which may be the same or different, are selected from the group R; and

Q<sub>3</sub> and Q<sub>4</sub> may be 0, 1 or more than 1 substituents that are individually selected from the group consisting of R<sub>12</sub>, a fused 5-membered ring or a 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from R<sub>13</sub>, and fused polyaromatic rings optionally substituted with one or more substituents selected from R<sub>14</sub> wherein R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub> are individually selected from the group R; and

R is the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted

aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted thioalkyl group.

2. An infrared dye composition comprising a molecule that can be described according to claim 1.
3. An infrared absorbing dye composition comprising a molecule in accordance to claim 1 wherein bulky substituents are utilized.
4. A solvent-based ink composition comprising a molecule that can be described according to claim 1.
5. A solvent-based ink according to claim 4 which is ink jet printer ink.

#### **ABSTRACT**

An infrared dye, characterised in that the dye comprises a compound that comprises a molecule that can be described by claim 1.

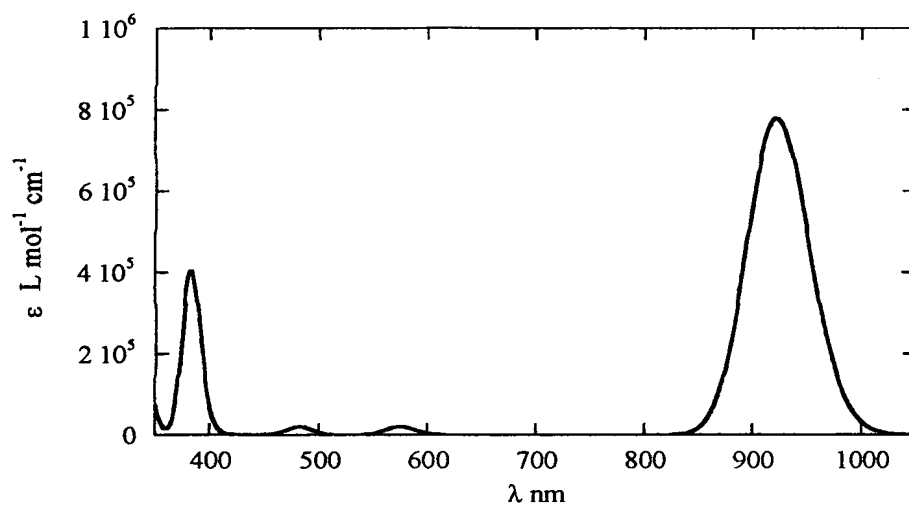


Figure 1: Calculated absorption spectrum for **3**

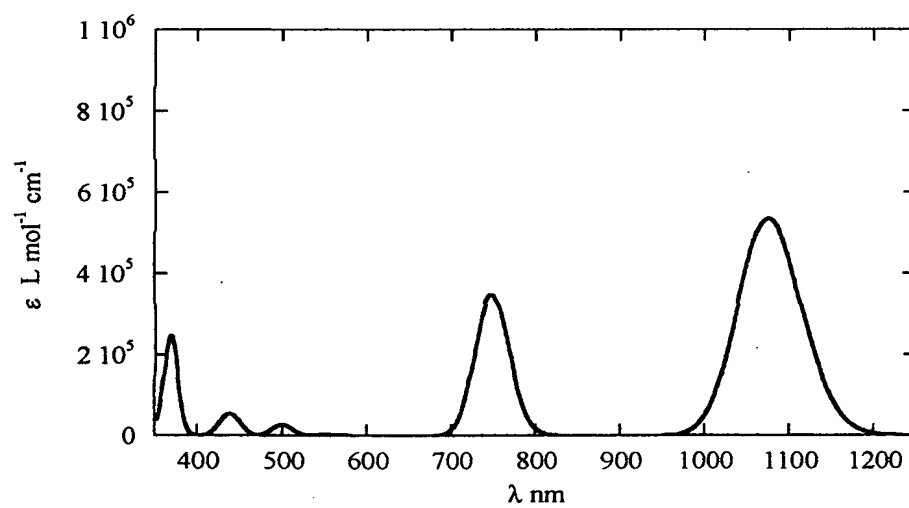


Figure 2: Calculated absorption spectrum for **4**

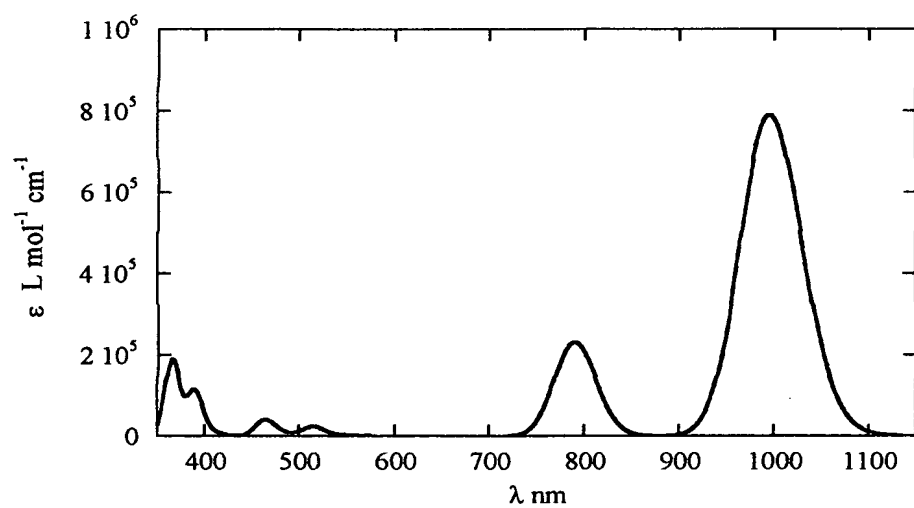


Figure 3: Calculated absorption spectrum for **5**

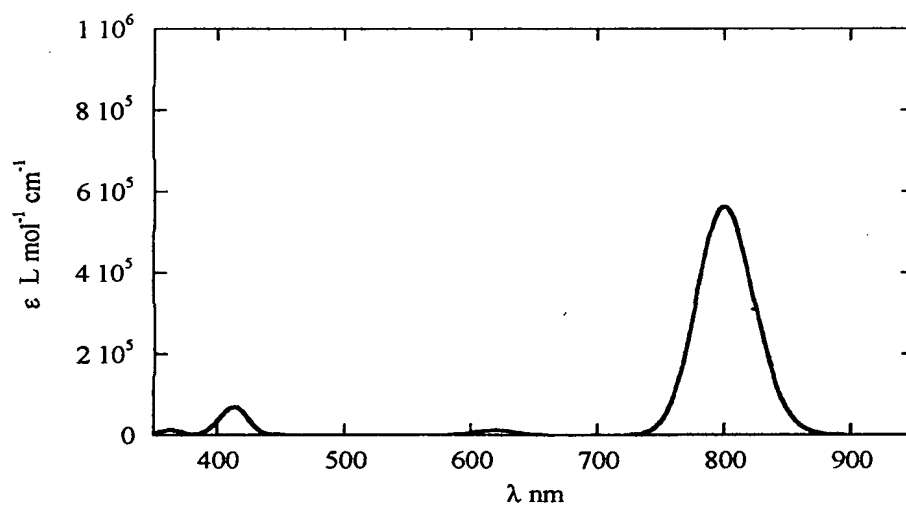


Figure 4: Calculated absorption spectrum for **6**

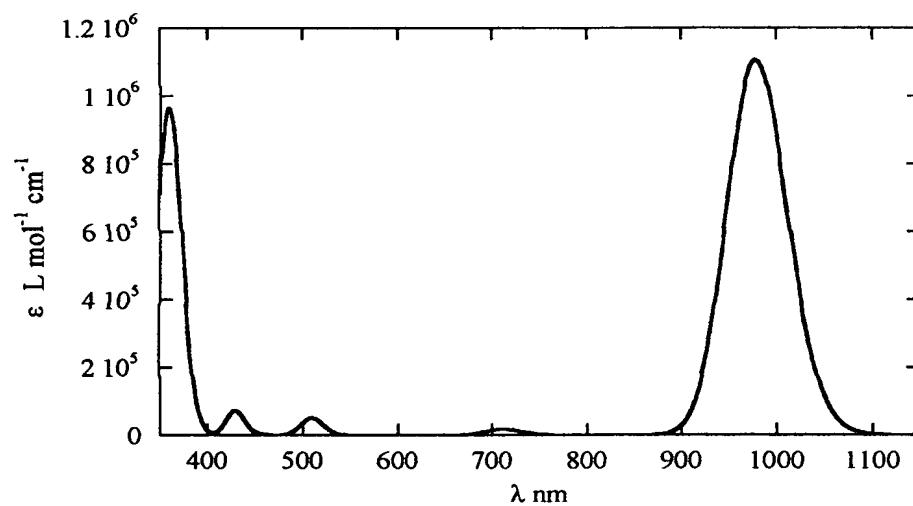


Figure 5: Calculated absorption spectrum for 7

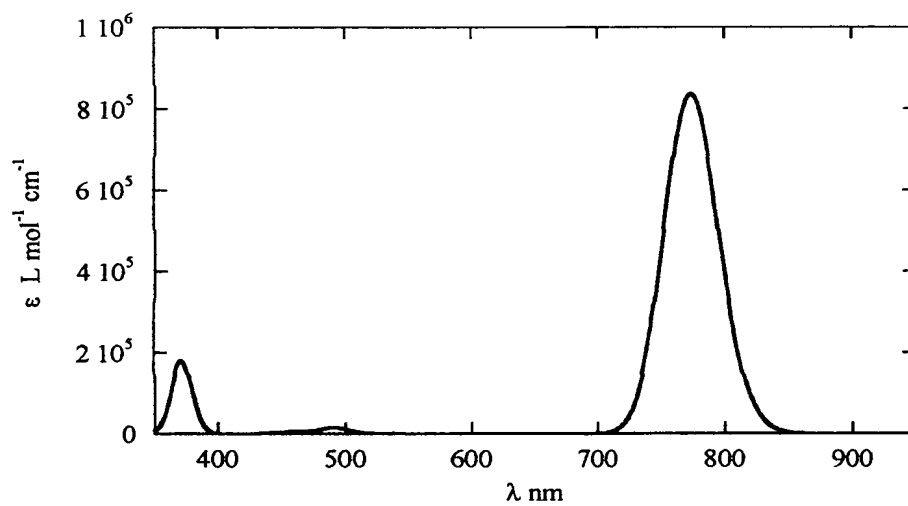


Figure 6: Calculated absorption spectrum for 8

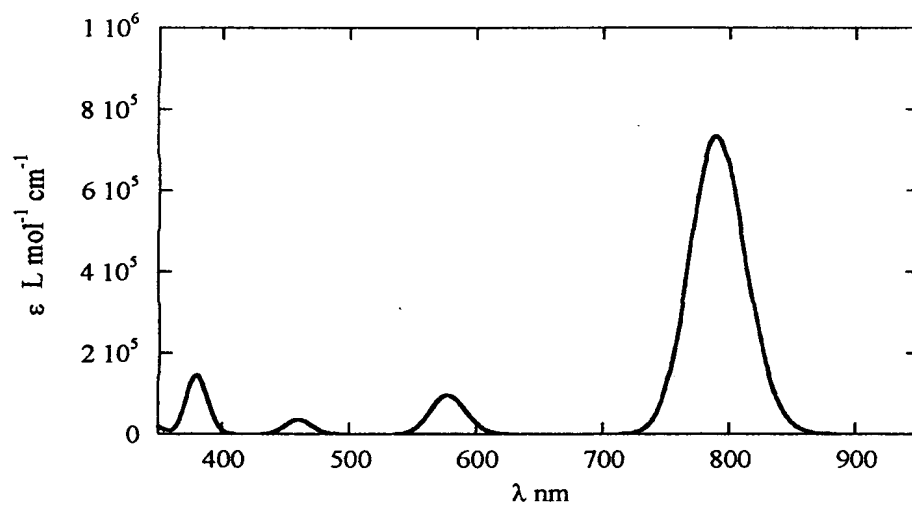


Figure 7: Calculated absorption spectrum for 9

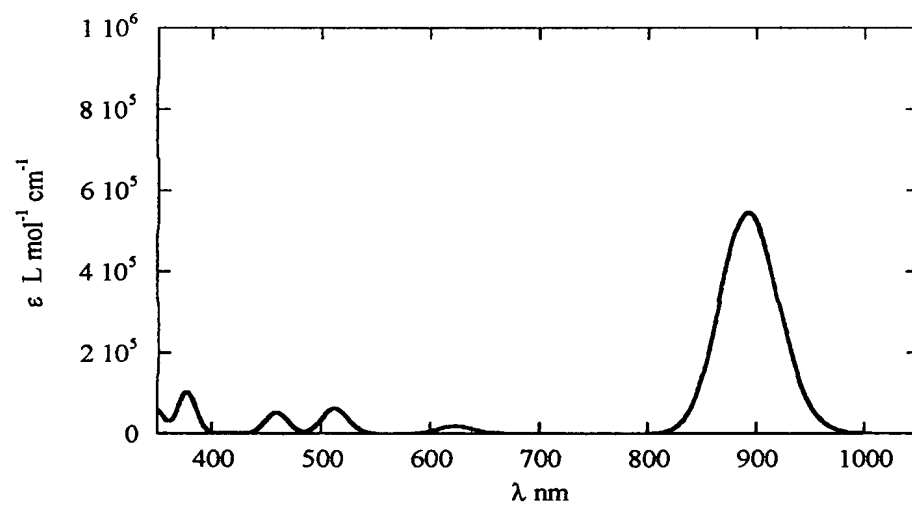


Figure 8: Calculated absorption spectrum for 10